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EFFECT OF PRESSURE AND TEMPERATURE ON THE SURFACE TENSION AND VISCOSITY

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EFFECT OF PRESSURE AND TEMPERATURE ON THE SURFACE TENSION AND VISCOSITY

FINAL REPORT
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EXECUTIVE SUMMARY

The development of the CANMET - Petro-Canada hydrocracking process is now well into the demonstration unit stage. As performance information accumulates, improved modelling of the process would be desirable. In order to make adequate use of such models, values of fluid properties at reaction conditions must be known. Of the many fluid properties, the viscosity and the surface tension of the liquid phase contribute one of the greatest degrees of uncertainty in the selection of reasonably correct values. The present study was undertaken to determine if these parameters can be predicted with acceptable accuracy, and if not, to evaluate experimental methods and to recommend which of these techniques may be the most suitable for use at the extreme conditions used in the CANMET process.

A review of existing theory, and of recommended empirical and semi-empirical correlations suggests that neither surface tension nor viscosity is likely to be accurately predictable at reaction conditions for the range of feedstocks likely to be used. In particular, values of the dynamic surface tension are difficult to predict.

A literature survey was done to examine published methods for measurement of surface tensions or viscosities. Those methods which could potentially be used at high temperatures (to 450°C) and at high pressures (to 17 MPa) were selected for further evaluation. The expected effects of pressure, temperature, time, and gas-liquid solubility equilibrium were summarized.

The maximum bubble pressure method for the measurement of dynamic and static surface tensions was selected as potentially the most suitable for the desired range of conditions. The drop formation method could also be used but was judged to be experimentally somewhat more difficult and less appropriate.

For the measurement of viscosity, the linear oscillation viscometer would be the first choice, on the grounds of ease of use and simplicity of construction. The method could also be adapted to measure fluid densities, as well as for use with suspensions. A second, but less desirable, choice would be the rolling ball viscosimeter.

RESUME EXECUTIVE

Le développement du processus de l'hydrocraquage de CANMET - Petro-Canada est à présent bien à l'étape de l'installation de démonstration. L'accumulation des informations de son fonctionnement fait désirable l'amélioration des méthodes de corrélation du processus. Pour que ces méthodes soient raisonnablement exactes certaines propriétés des fluides doivent être connues dans les conditions de réaction. De l'ensemble des plusieurs propriétés des fluides, ce sont la viscosité et la tension superficielle de la phase liquide dont les valeurs sont les plus difficiles à attribuer correctement. L'étude actuelle a été entreprise pour examiner si ces paramètres pouvaient être prédits avec la precision suffisante ainsi que pour reviser des méthodes experimentalles de leur détermination à fin de recommender lesquelles pourraient être adaptées dans des conditions extrèmes du processus de CANMET.

La revue de la théorie actuelle et des corrélations empiriques et semi-empiriques indique que ni la tension superficielle, ni la viscosité ne peuvent être raisonnablement prévues dans les conditions de réaction pour des matières d'alimentation qui seraient utilisées. Les valeurs de la tension superficielle dynamique sont particulièrement difficiles à prédire.

L'étude de litterature a été effectuée pour examiner des

méthodes publiées de mesure de la tension superficielle et de la viscosité. Des méthodes qui pourraient être potentiellement appliquées aux températures élevées (jusqu'à 450°C) et à haute pression (jusqu'à 17 MPa) ont été choisises pour l'examin ultérieur. Des effets attendus de la pression, la température, le temps et la solubilité gaz-liquide en équilibre ont été resumés.

La méthode de pression maximum de bulle a été jugée la meilleure pour mesurer la tension superficielle statique et dynamique dans les conditions desirées. La méthode de formation de goutte aussi pourrait être potentiellement appliquée mais elle parâit plus difficile et moins appropriée.

Le viscosimètre à oscilation linéaire grâce à la simplicité de construction et la facilité d'opération, semble le meilleur pour mesurer la viscosité. Cette méthode peut être aussi adaptée au mesure de la densité des fluids et aux suspensions. Le second choix, mais moins bon, serait le viscosimètre à bille roulante.

EFFECT OF PRESSURE AND TEMPERATURE ON THE SURFACE TENSION AND VISCOSITY

1.0 INTRODUCTION

The development of the CANMET hydrocracking process over the past decade has culminated in the current successful process demonstration unit now being operated in Montreal by Petro-Canada Ltd. at a scale of 5000 bbls/day. During the course of this development, pilot plant studies were continued in the Energy Research Laboratories of CANMET, and cold flow simulation tests were also performed in the Department of Chemical Engineering, University of Waterloo.

During this development work, as well as during fundamental studies, the need became apparent for values of the physical properties of the hydrocarbon systems under study. In particular, modelling of the hydrodynamic behaviour which controlled important reactor characteristics such as gas/liquid volume ratio, liquid residence time, liquid and solid mixing and solid concentration distributions required physical property values such as density, viscosity, surface tension, thermal conductivity, etc. The estimation of these properties, or their direct measurement, was made difficult by the severe reaction conditions used, that is, high pressure and temperature. In particular, estimated values for viscosity and surface tension suffered from a large degree of uncertainty.

The complex composition of the heavy feedstocks used in the CANMET hydrocracker also makes the estimation of physical properties a difficult task. In addition, some feedstocks contain surface active agents, and/or solid catalyst particles of varying size and density. In view of the problems in calculating values of these physical properties by the use of conventional correlations, it would be more satisfactory to measure directly those parameters of the most importance, or those which may be subject to large errors in prediction. For these reasons, a survey of methods for measuring viscosity and surface tension was undertaken. The latter property also includes the complexity of a possible time-dependency in systems containing surface active components, or in systems in which gas-liquid equilibrium has not been fully established.

2.0 OBJECTIVES

The program of work planned was initially proposed to be carried out in two phases. Phase I would survey existing equipment and methods and recommend those best suited for the measurement of viscosity, or of surface tension, or of both together, at pressures to 17 MPa and temperatures to 450°C. Phase II would then actually undertake these measurements if they were deemed to be feasible in light of the results of the Phase I study.

This report covers Phase I only, the objectives of which are itemized below.

1. Evaluation of existing equipment and techniques for their suitability to measure the surface tension of hydrocarbon oils at high pressure and temperature.

2. Evaluation of existing equipment and techniques for their suitability to measure the viscosity of hydrocarbon oils at high pressure and temperature.

3. More emphasis is to be placed on the measurement of dynamic surface tension than on the measurement of static surface tension.

4. Evaluate procedures, if suitable ones exist, which would allow the calculation of surface tension from other properties such as viscosity, density, refractive index, etc.

5. Provide a recommendation for the best methods available for both viscosity and surface tension.

It is not an objective of this study to critically review all existing literature on methods for the measurement of viscosity or surface tension. Rather, the literature will be surveyed to extract those publications of potential value in aiding in the accomplishment of the above objectives.

3.0 SURFACE TENSION

3.1 Review of Published Methods of Measurement

3.1.1 Introduction

Because surface tension is an interfacial phenomenon, anything that affects the properties of the interface will affect the value of the surface tension. For the measurement methods considered here, only a gas-liquid interface is involved. In a pure liquid, free of contaminants, surface properties depend on the nature of the fluid, and are not affected by the age of the surface. When contaminants are present, particularly when these have surface active properties, then the concentration of the contaminant in the interface may not be in equilibrium with that in the bulk fluid. If the interface exists for a sufficiently long time, the surface and bulk concentrations will come to equilibrium. Surface tension measurements made at equilibrium will yield the static surface tension value.

For very young surfaces, the surface adsorption process will not be at equilibrium and generally, the concentration of a surface active component in the interface will increase with time. As a consequence, the surface tension will change, normally decreasing, with time. Surface tensions measured for non-equilibrium interfacial concentrations are dynamic surface tensions, and they are functions of the age of the surface.

For very fresh or new surfaces, in liquids containing small amounts of surfactants, the measured surface tension will approach that of the pure liquid since there has not been sufficient time for transport and adsorption of excess reactant into the interface. At longer times (older surfaces) as surfactant accumulates in the interface, the measured surface tension will decrease to its final static value. In general, the change in the dynamic surface tension with time can be described by a diffusional model.

If time scales permit, it would probably be convenient to measure directly the change in surface tension with time for systems containing surface active components, and to obtain the static surface tension as the limiting value at long times, together with a time function applicable to each system of interest.

3.1.2 Range of Variables for Surface Tension

Before considering the probable ranges of the parameters of importance for hydrocracking, it is worthwhile to first briefly review the effects of temperature and pressure on surface tension in general and then summarize the expected behaviour of surface tension that might result when using hydrocarbon liquids at elevated temperatures and pressures.

Numerous methods have been developed to estimate the surface tension of pure liquid compounds and a comprehensive, critical review of many of these methods, together with the tabulation of

data for over 2200 compounds was prepared by Jasper (S-1). This work covers the literature from the 19th century through to 1969.

During this period researchers have made various attempts to correlate and to predict the surface tension of pure liquids. One of the more successful correlations is that of Macleod and Sugden developed in the early 1920's. Macleod (S-2) suggested a correlation of the form

$$\sigma^{1/4} = [P]\ (\rho_L - \rho_V) \qquad (1)$$

where ρ_L and ρ_V are liquid and gas densities, respectively, and is the static surface tension.

Sugden (S-3, S-4) called the temperature independent parameter [P], the parachor, a property that could be estimated on the basis of molecular structure. For a given system, and thus a fixed parachor, variation in surface tension is due solely to variation in the density difference of the two phases. Variation in surface tension due to changes in temperature and pressure are the result of the effect of the change of these variables on gas and liquid phase densities.

Efforts to produce a direct correlation between surface tension and temperature were many and varied. Goldhammer (S-5) provided a correlation for density differences in terms of easily measured properties

$$\rho_L - \rho_V = \rho_{Lb} \left[\frac{1 - T_r}{1 - T_{br}}\right]^n \qquad (2)$$

where $_{Lb}$ is the liquid density at the normal boiling point, T_r is a reduced temperature and T_{br} the reduced normal boiling point.

Combination of this expression with the correlation of Macleod and Sugden yields

$$= \left([P] \quad L_b\right)^4 \left[\frac{1 - T_r}{1 - T_{br}}\right]^{4n} \qquad (3)$$

The value of n varies from 0.25 to 0.31 depending upon the type of liquid with a value of 0.29 being recommended by Fishtine (S-6) for hydrocarbons. Numerous other correlations including one based upon the law of corresponding states (S-7) appear in the literature. In addition, one can find correlations between surface tension and various physical properties including refractive index (S-8), liquid compressibility (S-9) and viscosity (S-10 to S-14), all of which appear to be useful when working with pure liquids.

When one works with liquid mixtures, severe complications can be encountered. The surface tension of a liquid mixture is not a simple function of the surface tension of its pure components because the composition of the interface is not identical to that of the bulk phase. Under these circumstances, differences between static and dynamic values of surface tension can be significant, and this difference can be enlarged by the presence of small quantities of surfactants.

In general, the techniques available for the estimation of surface tension of mixtures can be used solely to predict values of static surface tension.

The predicted value usually exceeds the actual value. Predictions can be improved if experimental values of certain properties of the mixture are available. There does not appear to be any method available for the prediction of dynamic surface tension values for liquid mixtures. However, correlations for pure liquids are useful in attempting to describe the effects of temperature and pressure on the surface tension of mixtures, which are reviewed briefly below.

a) **Effect of Temperature**

The correlation presented as equation (3) indicates

$$\sigma \alpha (1 - T_r)^{4n} \tag{4}$$

Because the exponent, 4n, is close to unity one finds that a linear temperature dependency, of the form

$$\sigma = a + bT \tag{5}$$

proves to be adequate over a limited range $0.4 \leq T_r \leq 0.7$ (S-15). This simple relationship was shown to provide an adequate correlation between surface tension and temperature for complex mixtures such as tar sands bitumen (S-16) if the atmosphere was inert and saturated with bitumen vapour. Values of a and b are listed for pure compounds in Jasper (S-1). While this simple correlation may work in one case, it may fail in another, and with no theoretical basis it is difficult to generalize. In cases where temperature has a significant effect on the solubility of one or more of the components, it is possible that the

variation in surface tension with temperature will be completely opposite to that anticipated. Discussion of this aspect is continued later.

b) **Effect of Pressure**

On the basis of the Macleod-Sugden correlation given earlier one has

$$\sigma \propto (\rho_L - \rho_V)^4 \qquad (6)$$

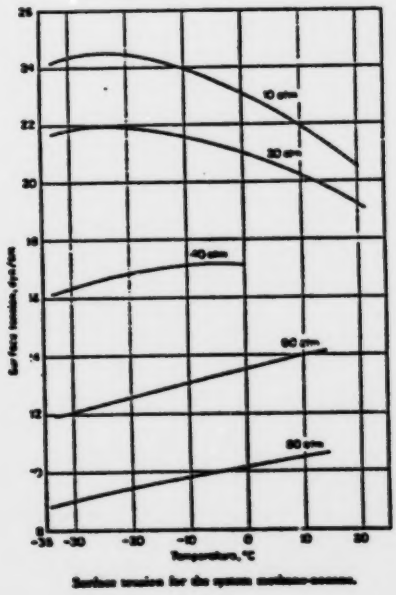
which indicates that for a pure-liquid, surface tension should decrease with increasing pressure (increasing ρ_V). At low pressures, where $\rho_L >> \rho_V$, σ will appear to be essentially independent of pressures. At elevated pressures, where the approximation $\rho_L >> \rho_V$ is no longer valid, a significant decrease of surface tension with increasing pressure is observed. Unfortunately, the behaviour of mixtures is much more difficult to predict. Here pressure, in addition to affecting densities, also influences solubilities which can result in significant changes in liquid and vapour composition.

In principle, the effect of pressure on the value of the surface tension for a pure liquid is related to the change of volume with pressure, and can be estimated from that relationship (S-17).

c) **Effect of a Change in Solubility**

In a multi-component system where the equilibrium compositions of the gas-liquid components show significant changes, one to the other, with respect to temperature and/or pressure, large

changes in surface tension can result. Such changes cannot be predicted unless extensive thermodynamic data are available. A good example of solubility effects is provided in the work of Deam and Mattox (S-18), illustrated graphically below. They investigated the surface tension of methane-nonane mixtures over the temperature range -34° to 24°C for pressures between 1 and 100 atm. While for any temperature, surface tension was observed to decrease with increasing pressure, the effect of temperature variation produced unexpected results. At the lower pressures the anticipated decrease of surface tension with increasing temperature was observed while at the higher pressures a complete reversal was noted. This phenomenon illustrates that the change in solubility of methane in nonane and the resulting change in the liquid phase composition has a far greater effect on the surface tension than the effect of temperature alone.



For the hydrocarbon liquids suggested for study in this project, surface tension values would be expected to vary from about 1 to 35 dynes/cm. (Note: An equivalent SI unit is 10^{-3} N/m.) A value of 35 dynes/cm is about as high as would be expected for any hydrocarbon compound at room temperature. Since the value of surface tension will decrease with increases in both temperature and pressure, at the limit of 450°C and 17 MPa, very low values are to be expected, depending on the composition of the gas and vapour phases but in all liklihood, of the order of 0 to 5 dynes/cm.

3.1.3 Review of Methods for Measurement of Surface Tension

Only methods for the measurement of the dynamic surface tension will be evaluated because it is assumed that the static surface tension can also be obtained from the same results, either by making measurements at long times or by extrapolation of dynamic surface tension values to long times.

Five main types of measurements may be made to determine the dynamic surface tension, and these are described briefly below.

a) **Liquid flow methods** - One such approach depends on the mechanical instability in a jet of the test solution emerging from a non-circular orifice. The stream oscillates around a circular cross-section shape. Complex expressions are required to relate surface tension to node-node spacing or wave-length. Jet dimensions as

they change with time must be obtained optically, and they are awkward to measure and imprecise. Surface ages are very short with this method. Another liquid flow technique depends upon the relationship between surface tension and the shape of a falling column of liquid. Surface tension opposes the elongation produced by accelerated motion and the consequential cross-sectional area constriction. Control of the flowing column tends to be difficult and precise measurement is also needed, with optical methods required.

b) **Capillary waves** - The wavelength of ripples on the surface of a test solution is related to the surface tension. A complex formula is required to extract the actual result. This method has met with relatively little acceptance.

c) **Wilhelmy plate** - This method determines surface tension from the force required to pull a plate or cylinder vertically away from the test solution surface. While this is an adaptation of the normal force balance ring method, it can be further exploited to yield dynamic surface tension values as well by oscillating the plate through the surface and recording the resultant forces accompanying the compression and stretching of the surface film (S-19). Another version of the oscillating plate has also been described by Nissen (S-20) which was used to measure viscosities and static surface tension. However, the apparatus described could probably be adapted to measure dynamic surface tensions as well. Very short surface ages do not appear to be feasible with

this method with respect to dynamic surface tension measurements. The method requires mechanical drives which could cause some experimental difficulties at high pressure or temperature. An example of this kind of apparatus is shown in Figure 1 (S-19).

d) **Pendant Drop methods** - This method relies on the relationship between the volume of a drop formed at the tip of a capillary and its surface tension. When drop sizes are measured, normally by optical means, a value of the static surface tension is obtained. In order to obtain dynamic surface tension values, a continuous stream of drops is formed. If the flow rate is accurately measured and the drops per second counted, then drop volumes can be calculated and the surface tension determined. A number of separate tests at different flow rates are required to establish the variation of the surface tension with time. Because of the time required to form a drop, surface ages with this method will be several seconds or more. However, the method is precise (but see "Discussion" for other aspects). This method was used by Hwang et al. (S-21) to measure the static surface tension of various coal liquids at high pressures and temperatures. Apparently, no attempt was made to use the apparatus for dynamic surface tension measurements. A diagram of their apparatus is shown in Figure 2. Presumably, by using the methods described by Kloubek et al. (S-22), dynamic surface tension values could be obtained.

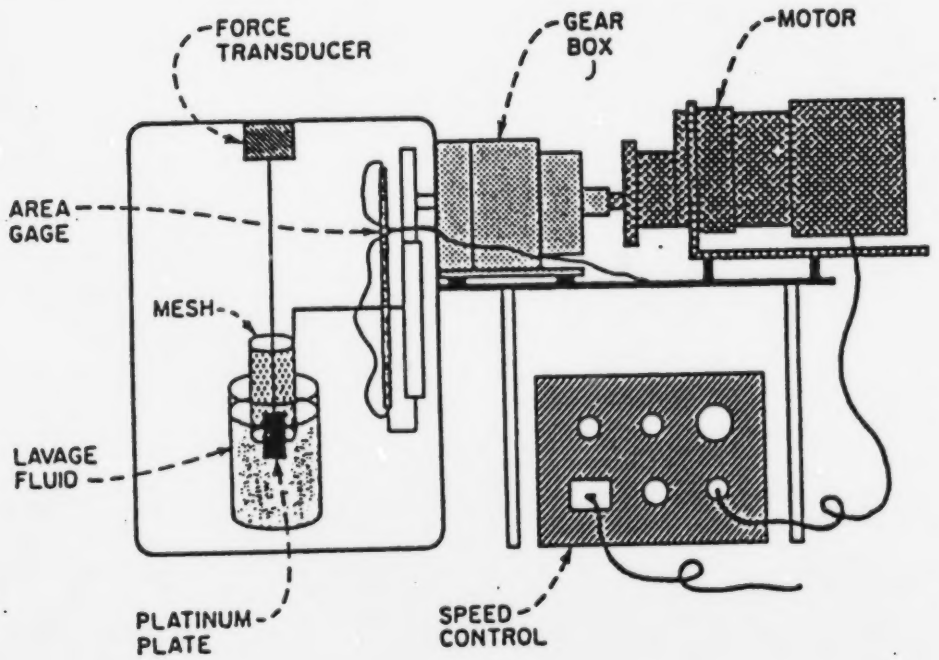


Figure 1 A schematic drawing of the surface balance showing the drive mechanism, mesh cylinder and hypophase breaker. The film balance is enclosed in a thermostatically regulated chamber so that temperature and humidity can be controlled (S-19)

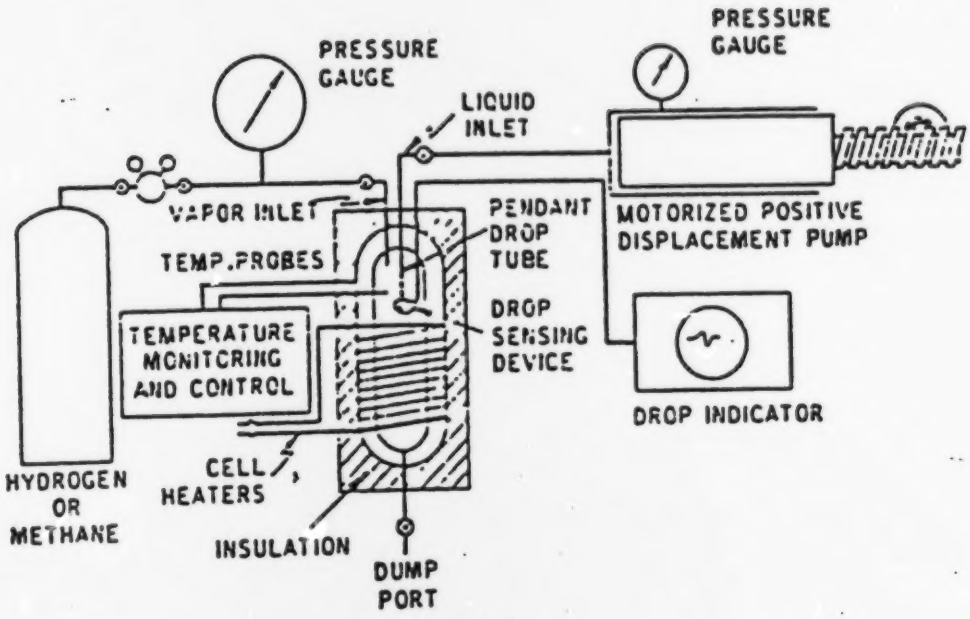


Figure 2 Schematic of surface tension measurement apparatus (S-21)

e) **Maximum bubble pressure method** - This method depends on the fact that the inflation pressure for a bubble forming at an orifice is at maximum when the bubble achieves minimum radius of curvature. This occurs as it assumes a hemispherical shape (so that bubble radius equals orifice radius) at the gas orifice. For small orifices, this maximum pressure and minimum radius are related by a simple expression to the surface tension, that is, $\sigma = \frac{pr}{2}$, where σ is the surface tension, p is the pressure difference between the orifice pressure external to the bubble, and r is the radius of the orifice. The principal advantages of this method are that it can be readily adapted for high temperatures and pressures, and that it is possible to measure transient surface tension values from almost zero times to times long enough to approach equilibration.

However, at very slow bubbling rates, some imprecision can cause scatter of the values to some degree (S-23). Bubble frequencies can be obtained from the pressure fluctuations as bubbles are formed. A diagram of one version of a maximum bubble pressure apparatus is shown in Figure 3 (S-24). An example of bubble pressure recording traces is given in Figure 4 (S-25). A rather unique modification of the bubble pressure method was proposed by Lukenheimer et al. (S-26). Here two containers are used, one of which contains a reference liquid. However, it is necessary to measure changes in the bubble dimensions with time, and this could present experimental difficulties.

Other specialized methods have been proposed for the measurement of static or dynamic surface tensions, but these did not appear to be practical at high temperatures or pressures, or were not

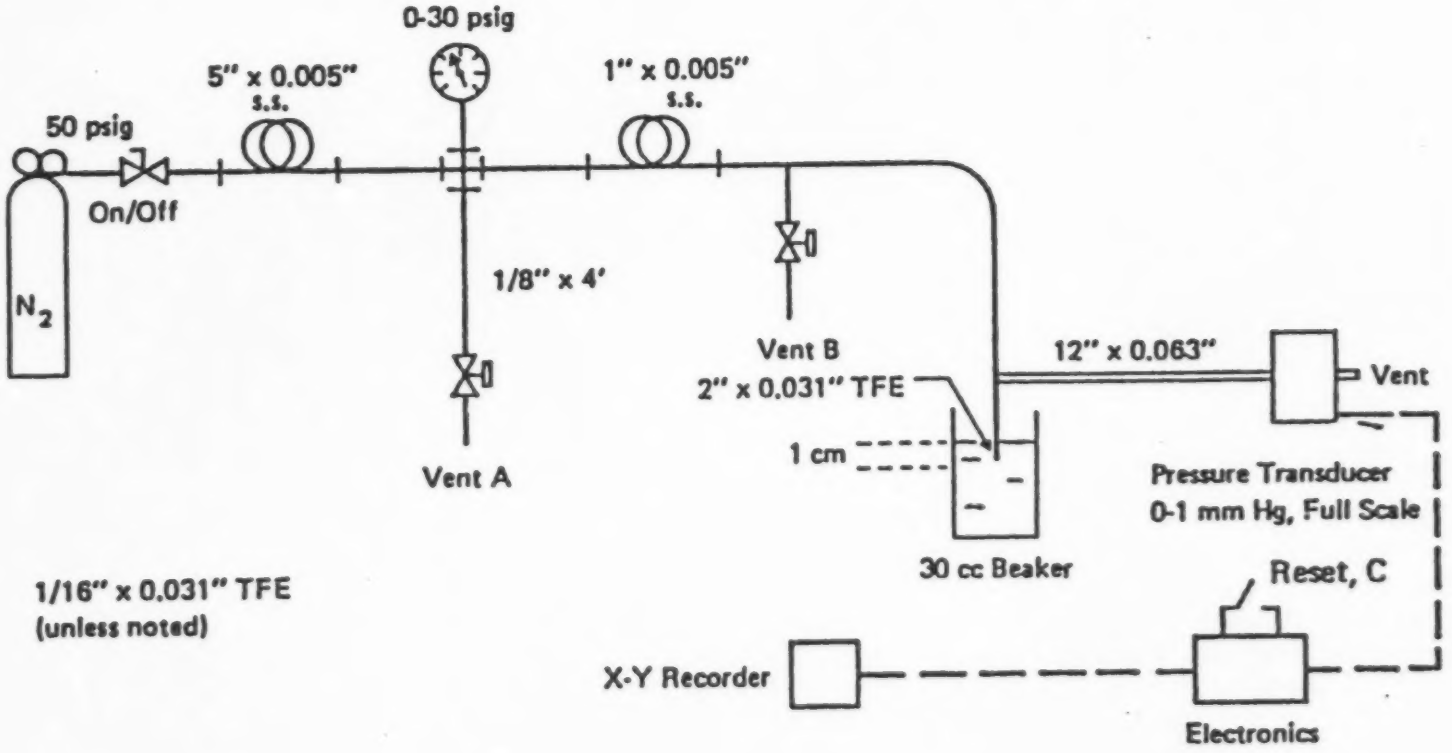


Figure 3 Dynamic surface tension apparatus (S-24)

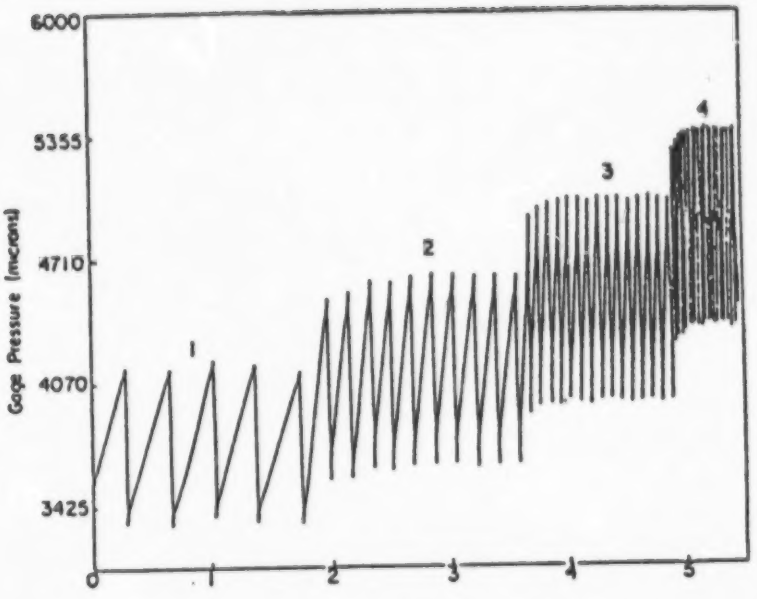


Figure 4 A strip chart recorder trace showing the pressure as bubbles are being formed and released for four different flow rates. Data are for a 0.0022% aqueous solution of $C_{12}E_4$ with an equilibrium surface tension of 32.2 dynes/cm. Dynamic surface tensions for the four average times shown are 52.6, 58.6, 63.6 and 68.2 dynes/cm corresponding to adsorption times of 22.5, 13.6, 5.3 and 1.1 sec, respectively (S-25)

convenient for use on the type of liquids intended to be studied in the proposed work.

For example, capillary rise methods require an optical means of measuring the location of the meniscus, and some knowledge of contact angle (wettability). While pressure cells having windows have been used for surface tension measurements, these have yielded static values only, and the temperature range has been restricted by the materials needed to obtain visibility. Also, it has been reported that it is very difficult after the first experiment to measure the meniscus position for dark liquids that wet the capillary.

The same concerns about the need for optical measurements applies to pendant drop methods or to bubble growth methods, in which direct measurement of drop or bubble dimensions is necessary. Other dynamic methods based on flow visualization such as oscillating jets, capillary surface waves or falling films would be very difficult to operate at high pressures and temperatures, and simpler techniques appear to be available. Also these flow methods generally involve very short (milliseconds) surface ages - much shorter than might be expected in a bubble column. Rather complex mathematical treatment of data is also required to obtain surface tension values.

4.0 DISCUSSION

Of all the numerous methods described in the literature, two would appear to have the greatest potential for the successful measurement of dynamic surface tensions at high pressures and temperatures. These are what might be called the "stream of drops" method and the "stream of bubbles" method (or maximum bubble pressure method).

The stream of drops method requires drop counting, either visually or by means of a drop-detection sensor, as well as precise flow measurement of small liquid quantities. A high pressure syringe-type pump is often used to supply liquid to the test capillary at a controlled constant rate. However, this rate must be variable to yield data at a sufficient number of flow rates to allow extrapolation of the data to zero flow. The small drop sizes require that corrections for vaporization and for buoyancy be made, which means that gas and liquid densities and compositions must be known. At fast drop rates, equilibration between the ambient vapour phase and the liquid in the drops may not be achieved. While the liquid could be pre-equilibrated with the vapour, this might require that the pump be filled at high temperatures and pressures, and be kept at these conditions. Such pumps would not likely be operable at temperatures even as high as 200°C. For the drop method, each point on a surface tension vs. time (surface age) plot requires an independent experiment, which is not the case for the maximum bubble pressure method. On the other hand, Kloubek (S-23) claims that the extrapolation of the surface tension-time curves to infinite time (from a plot of 1/time vs. surface tension) to obtain a static value

is more accurate with the drop method than for the bubble method. However, the bubble method can cover a wider range of surface ages than can the drop method.

For either the drop or bubble method, the surface age is related to the rate of formation of the drop or bubble at an orifice. For a bubble column however, the bubble-liquid interface continues to alter in surface tension over much of the time the bubble is rising through the liquid. This behaviour has been observed experimentally, for example, in a foaming system the depth of foam is directly proportional to the depth of liquid, that is, to the time of bubble rise (S-28). Further, in foaming systems with even mild foaming tendencies, the bubble sizes and rise velocities change over several metres of column depth above the sparger orifices. It appears that some foaming hydrocarbon systems may be slow to equilibrate, and surface age times of up to 60 seconds or so may be of importance.

The maximum bubble pressure method requires close control of gas flow rates and a sensitive differential pressure measurement. However, the method needs no moving parts, and the measurement systems can be isolated from the high temperatures. The method would seem to simulate very well the mass transfer-adsorption processes that might be occurring in a bubble column, in that the surfactant diffusing from the liquid to the newly formed interface is available from what is, in effect, an infinite reservoir, in contrast to the gradients which might potentially occur in a small liquid drop. By making measurements at increasing values of flow rates, a plot of dynamic surface tension vs. surface age can be obtained in one experiment. By pre-saturating the liquid in the

bubbling reservoir, equilibrium between gas and liquid can be assured at the temperature and pressure of the experiment. On the other hand, Kloubek (S-23) claims that some error may occur at very slow bubbling rates because of retention of liquid in the gas orifice capillary, or because of imperfect wetting. An absolute calibration would be desirable for these reasons, as well as to allow for dimensional changes in the orifice at different operating conditions. This latter precaution would also be required for the drop method, however.

5.0 CONCLUSIONS AND RECOMMENDATIONS

In summary, it would appear that the maximum bubble pressure method should be the first choice for the measurement of dynamic and static surface tensions. Some of the problems described by Kloubek (S-23) encountered with the maximum bubble pressure method were not apparently experienced by Bendure (S-25) for bubble ages in the range of 1 to 100 seconds, which is within the range of interest for bubble columns. Similarly, the recent report by Miller and Meyer (S-24) on their use of the maximum bubble pressure method does not mention or show at bubble ages from 0.1 to 1.0 second any of the lack of precision described by Kloubek. Hence, it appears that this method should give good results for dynamic and static surface tension measurements, and that values should be obtainable over the entire range of temperature and pressure of interest. In addition, the method should be employable even with slurries, although there is no evidence that the presence of solid particles will affect the values of vapour-liquid interfacial tension measurements.

There is little liklihood of predictive methods being of wide general use for surface tension values. At present, recommended methods require knowledge of critical values or of parachors, neither of which is likely to be readily available for the complex type of hydrocracker feedstocks of interest. Also, correlations presently recommended are only for the prediction of static surface tension values (S-15, S-27). As far as is known, there is no present way to predict dynamic surface tensions, although some correlating methods based on diffusional models have been suggested.

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6.0 VISCOSITY

6.1 Introduction

A Newtonian fluid is one in which the shear stress γ is directly proportional to the shear rate (velocity gradient) du/dy:

$$\gamma = \mu du/dy$$

where the constant μ is known variously as the coefficient of viscosity, the absolute viscosity or the dynamic viscosity. If this linear relationship does not hold the fluid is non-Newtonian in which case μ varies with the rate of deformation. Non-Newtonian fluids include those for which the apparent viscosity is a simple function of the shear rate, those which show time-dependent behaviour such that the shear stress changes with time at constant shear rate (e.g. thixotropic fluids) and viscoelastic fluids which show elastic as well as viscous properties (e.g. "crazy putty").

The usual unit of viscosity is the Poise. 1 Poise = 1 dyne cm^{-1}. For low viscosity fluids the centipoise (cP) is more convenient. The SI equivalent is Pa s

$$1 \text{ cP} = 1 \text{ m Pa s} .$$

For example, water has a viscosity of 1 cP at 68.4°F. The ratio of the absolute viscosity of a fluid to that of water at 68.4 is called its specific viscosity. The ratio of the absolute viscosity of a fluid to its density is the kinematic viscosity. If viscosity is in Poise and density in g cm^{-3}, the corresponding kinematic viscosity is in Stokes

$$1 \text{ Stoke} = 1 \text{ cm}^2 \text{ s}^{-1}$$

Viscosity is generally a weak function of pressure but a very strong function of temperature. The viscosity of a crude oil or a residuum can vary by several orders of magnitude over a range of a few hundred °C, the particular range depending on its specific gravity (see Figure 1). For temperatures of 400° to 450°C, expected viscosities are of the order of 1 cP. On the other hand increase of pressure from 0 to 2000 psi is expected to increase the viscosity by not more than 30 to 40%.

Fortunately, hydrocarbon oils seem to show Newtonian behaviour over the whole range of conditions of temperature, pressure and shear rates likely to be encountered in a hydrocracker. For instance, there is data indicating that hydrocarbon based lubricating oils begin to show non-Newtonian behaviour, in the form of decreasing viscosity coefficient, only at shear rates of the order of 10^4 s^{-1}, corresponding to shear stresses of the order of 10^3 N m^{-2}. This means that the search for a suitable method of measurement need not be restricted to those which permit controlled variation of shear rate. (If the temperature is such that pitches begin to form by dehydrogenative condensation to large polyaromatics so that a liquid crystalline mesophase is present, then thixotropic non-Newtonian behaviour in which the shear stress decreases with time at constant shear rate is likely to be observed.)

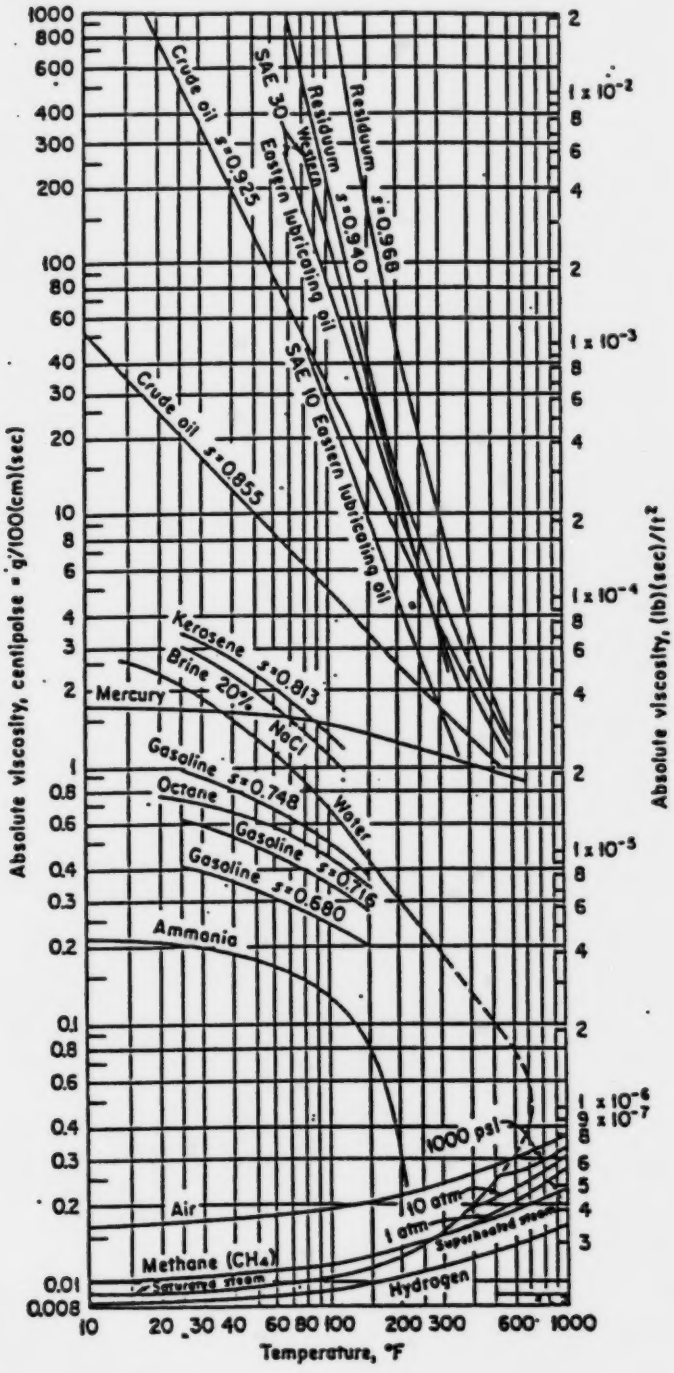

Figure 1 Values of Absolute Viscosity

6.2 Review of Methods of Measurement of Viscosity

Viscosity may be measured in principle by any method in which the fluid is subjected to shearing stresses. A wide variety of techniques are in fact practised, most of which have been adapted for measurement at high temperature and/or pressure. They may be classified into the following broad classes though it should be stressed that the details of implementation vary considerably within each class.

(a) Falling body methods

(b) Rotational methods

(c) Capillary flow methods

(d) Oscillatory methods

Each of these will be discussed in turn.

(a) **Falling body methods:** These include guided or free-fall falling ball, falling cylinder and rolling ball methods. Of these the rolling ball appears to be the most widely used for study of viscosity under severe conditions. The method involves the measurement of the constant velocity of a ball rolling down an inclined tube filled with the liquid under investigation. It has the advantage that only small samples are required. The fundamental basis for the method was established by the extensive studies of Hubbard

and Brown [V2]. They showed that the viscosity is given by

$$\eta = \frac{K}{L}(\rho_b - \rho)\cdot\sin\theta\cdot t \qquad (1)$$

where K is a calibration constant, L the distance over which the ball rolls in time t, θ the angle of inclination and ρ_b and ρ the densities of the ball and liquid respectively. This relation is only valid in the region of laminar flow of the fluid which is that region in which the Reynold's number Re is less than about 50.

$$Re = \frac{Ld^2\rho}{(D+d)\ t\eta} \qquad (2)$$

(D and d are diameters of tube and ball respectively.) However Hubbard and Brown have shown how to correct data taken in the turbulent region. K is nominally a function of d/D but a small dependence on θ has recently been established [V3].

K, ρ_b and ρ all vary with temperature so the apparatus must be calibrated at each temperature or the temperature effect estimated from the formulae given by Hubbard and Brown.

There are several problems to be overcome in adapting the method for high pressure and temperature. The ball may be returned to its starting position by tilting the whole assembly, requiring that flexible connections be made to the pressurizing manifold. This is illustrated in Figure 2 which shows the viscometer of Hwang et al. [V1]. The ball is constructed of ferromagnetic steel and the

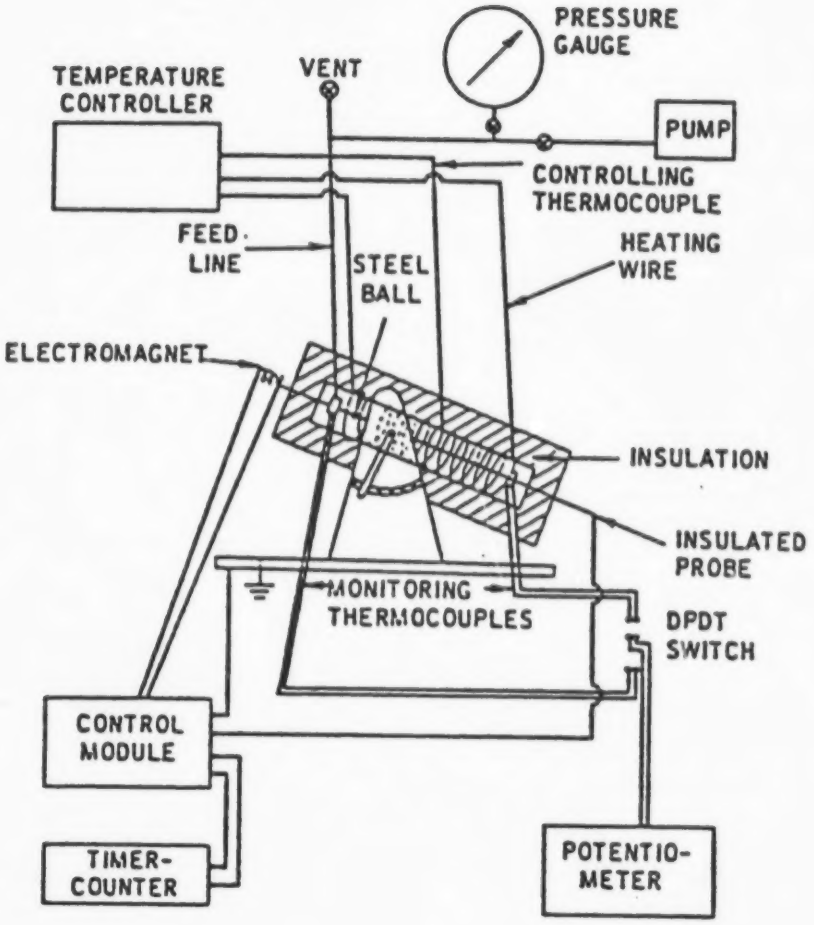

Figure 2 Schematic of Viscometer and Associated Apparatus

viscometer tube of non-magnetic stainless steel. High sphericity of the ball and uniformity of the tube ($\cong \pm 2\ \mu m$) is required with $d/D \cong 0.92$. The ball is retained in its starting position by an external electromagnet. On release a timer is started which stops when the ball closes a circuit by making contact with a platinum tipped probe electrically insulated from the guide tube.

An appreciable source of error in this arrangement is the inability to time the motion of the ball only after it has accelerated to constant velocity. Typical measuring distances L are $\cong$10-20 cm while constant velocity is attained within 2-3 cm of the start. The acceleration distance will in fact vary with liquid density and viscosity so the use of an average velocity over the whole length of tube may induce errors of several percent. For low temperature work the position of the ball can be measured inductively by a differential transformer in close contact with the tube and positioned an appropriate distance down the tube. For instance see the apparatus of Nishibata and Izuchi in Figure 3. Unfortunately this option is not available for high temperature work on account of the possibility of breakdown of the electrical insulation of the transformer coils.

As shown by equation (1) data on fluid densities are also required. Hwang et al. [V1] solved this problem by construction of a separate apparatus (shown in Figure 4) for density measurement. With it the density is determined from the volume of liquid displaced from

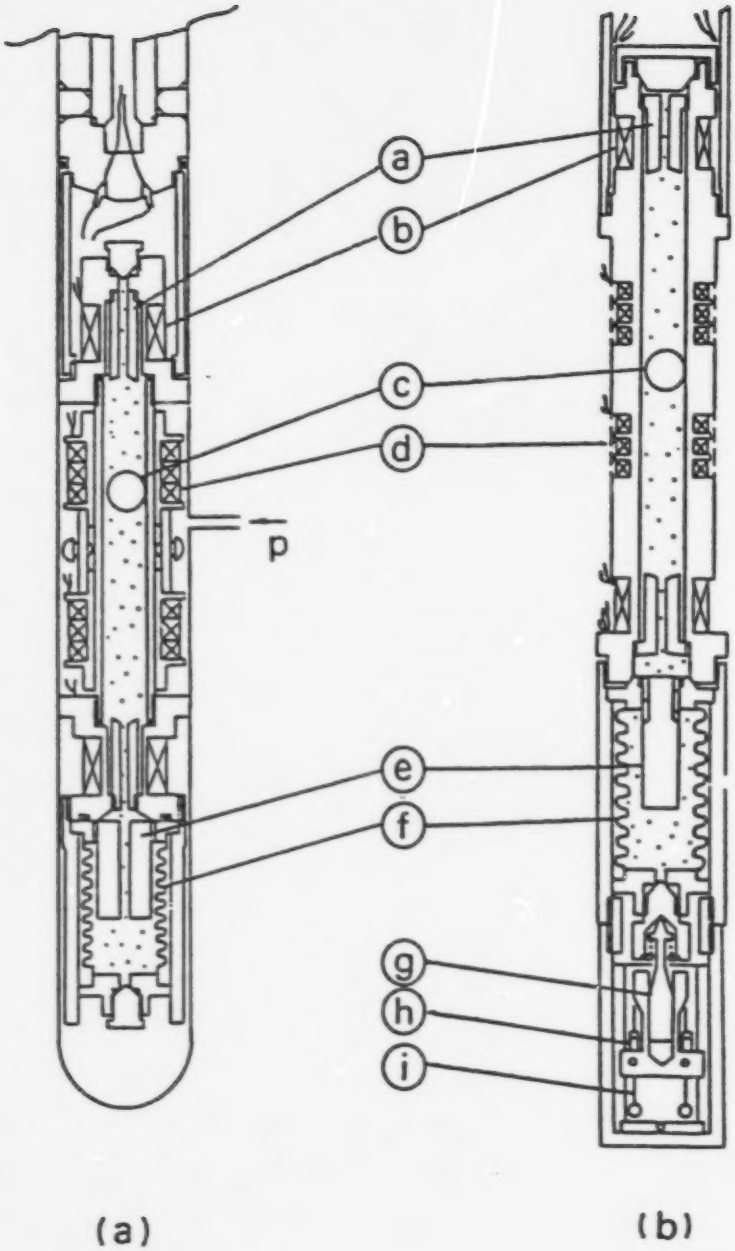

Figure 3 Viscometer cells of original design (a) and of improved design assembled with the potentiometer (b); a = permalloy cylinder; b = retaining coil; c = ball; d = differential transformer; e = spacer; f = bellows; g = connecting stem; h = leaf spring contact; i = manganin wire.

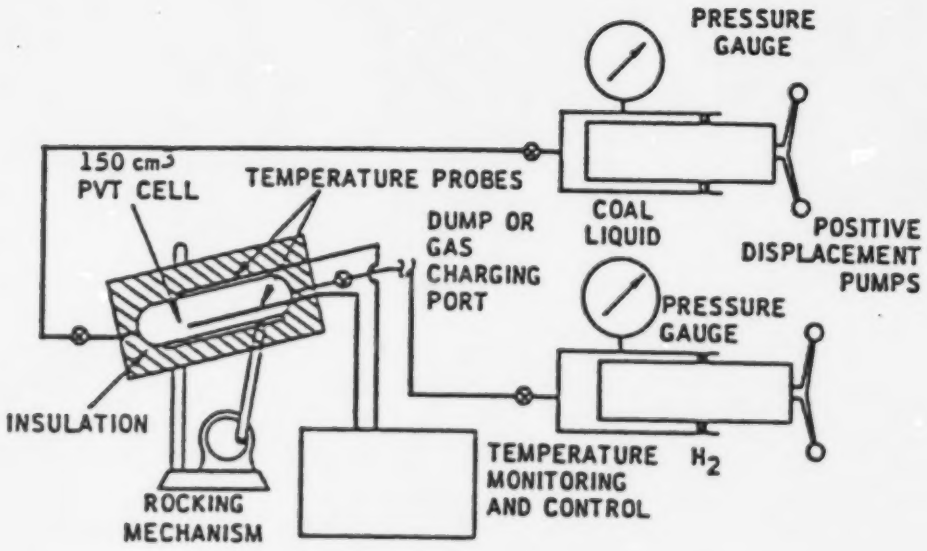

Figure 4. Schematic of density measurement apparatus.

an autoclave cell of known volume. The pump must be such as to enable volumetric displacements to be read to ± 0.01 cm^3, from a cell of $\simeq$ 100-200 cm^3. Corrections must also be made for the compressibility of the pump/manifold assembly which must be measured separately. A more elegant solution often used is to attach, directly to the viscosity tube, a bellows the extension of which can be measured by a differential transformer or by a variable linear potentiometer as used in the apparatus shown in Figure 3. Once more however this option does not appear to be viable for high temperature work on account of material limitations on the bellows.

In summary then, the principal advantage of the rolling-ball method is its relative simplicity and the extensive information available on its performance. Drawbacks include the rather extensive calibration required over temperature, pressure and roll angle. There is also the possibility that thermal decomposition of the fluid at more extreme temperatures may cause deposition on the tube and ball, but this is offset by the ease of disassembly for cleaning. The other drawback is the apparent necessity for a separate apparatus for density determination.

The use of a free-falling ball may seem to be preferable since it is possible to obtain an absolute viscosity without the need for calibration, viz.

$$\eta_s = \frac{1}{18}(\rho_b - \rho) g d^2 \frac{L}{t} \qquad (3)$$

where η_s is the viscosity according to Stokes' Law. Absolute

viscosities are then obtained by applying a known correction (Faxén's correction) involving the relative diameter of the tube and ball (V2). However for low viscosities like those used here a long tube which must be kept at constant and uniform temperature is required. This may be difficult to achieve.

(b) **Rotational Methods:** Rotational viscometry may be implemented in several different configurations. Perhaps the most common involves placement of the fluid between two concentric cylinders. One may then rotate either of the cylinders at a known speed and measure the torque on the other, which remains stationary.

A serious problem is maintenance of the correct alignment of the cylinders at all temperatures and rotational speeds. This will inevitably require contact points at which frictional losses will lower the sensitivity. No applications involving the accurate measurement of viscosities less than about 10 cP at high pressures have been found. Accordingly, although these methods are attractive because (i) they enable absolute viscosity determination (after correction for end effects), (ii) they allow controlled variation of the shear rate, (iii) they offer no difficulty with suspensions, and (iv) they do not require independent measurement of the fluid density, they will nevertheless not be considered further.

Similar criticism applies to the "cone and plate" method of the type used in rheogoniometry.

(c) **Capillary-Flow Methods:** Here the fluid is forced through a long smooth cylindrical narrow-bore tube under laminar flow conditions by the application of a hydrostatic pressure differential across the tube. The method is precise and has a rigorous theoretical basis. The configuration may involve either the free fall of the liquid under the influence of gravitational forces or its forced displacement through the capillary by the use of moveable pistons.

There are however several difficulties for the present application. First is the maintenance of constant temperature along a significant length of capillary tubing. Secondly, on account of the small bore of the tube the problem of deposition on the walls and cleaning of the tube by a method which maintains its high smoothness becomes severe. Thirdly the pressure drop across the capillary will in general be substantial so that dissolved gases may be released unless the pressure on the efflux side is carefully controlled. These defects seem substantial enough to eliminate these methods as well.

(d) **Oscillatory Methods:** Once more there is a great variety in the manner of application of these methods but in general they involve measurement of the damping of the vibrations of a body by the viscous drag exerted on its surface by the fluid in which it is immersed. The following are some of the variants of the technique which have been adapted for the high temperature/high pressure regime.

(i) The damping of the torsional oscillations of a horizontal circular disc suspended in the fluid by a torsion wire. While high sensitivity can be achieved the apparatus is complex and delicate and the theory rather difficult.

(ii) The damping of the torsional vibrations of a quartz crystal. This method is attractive in that there are no macroscopically moving parts but it is necessary to incorporate the crystal in a tuned circuit to allow measurement of the shifts in impedance and resonant frequency when the crystal is immersed in the fluid. This is non-trivial. Furthermore the theoretical analysis is still somewhat uncertain involving as it does a coupling between piezoelectricity, elasticity and fluid methanics.

(iii) The oscillating cup method in which the liquid contained in a cup suspended from a torsion wire and damps the torsional motions of the cup. The method is difficult to implement and the theoretical analysis is cumbersome.

(iv) The damping of the ultrasonic vibrations induced in a thin metal strip by magnetostriction. This method is quite effective and suitable but is electronically more complex than the following which is a variant of it and which has other advantages as well.

(v) The damping of the linear oscillations of a plate suspended in the fluid from a helical spring. This is the preferred method and will be described in more detail.

Linear oscillation viscometers have been discussed by White and Solomon [V4](see Figure 5) and by Nisson [V5](see Figure 6) among others. A thin flat plate suspended vertically in a fluid obeys a simple form of hydrodynamic equation for Reynold's numbers $Re \lesssim 10^5$.

$$Re = Vb\rho / \eta$$

where V = linear velocity, b = breadth of plate perpendicular to the direction of motion, ρ = fluid density and η = fluid viscosity. For the low frequencies ($\cong$2 Hz) and for the thin plates ($\cong$0.2 mm thick) useful for low viscosity fluids, this condition is easily met.

The plate is suspended from a quartz or steel spring with a reasonable range of elastic extension. Higher up on the same suspension is the ferromagnetic core of a linear variable differential transformer which gives an output directly proportional to the vertical displacement of the core from its null position in the surrounding coil. The suspension wire passes through baffles which serve to protect the coil from the furnace which can easily be arranged to be separated by over 30 cm. Provision must be made for adjustments to centre the core of the transformer. The fluid under test is contained in a small crucible of a few cm^3 capacity supported on a pedestal which may be arranged for either manual or motorized raising and lowering.

The suspension is set in oscillation by applying a short dc pulse to the secondary of the transformer. The ac output is then measured. The oscillation decay curve (see Figure 7) has an envelope whose

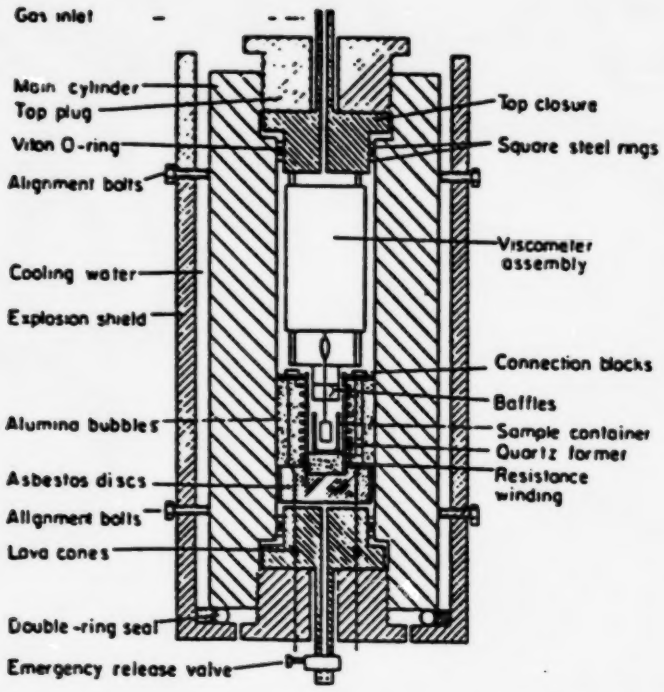

Figure 5a High Pressure Vessel with Furnace and Viscometer Assemblies

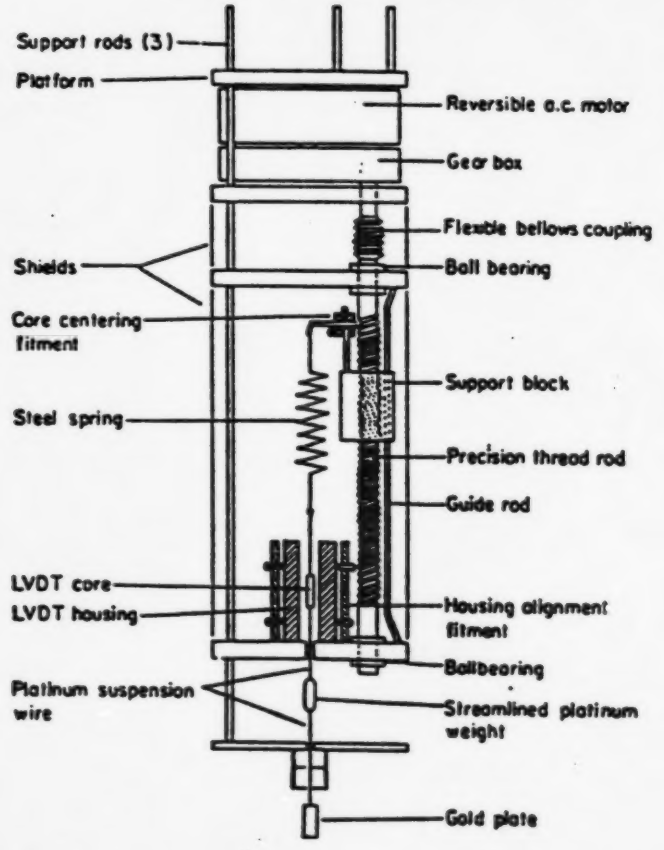

Figure 5b Details of Viscometer Assembly

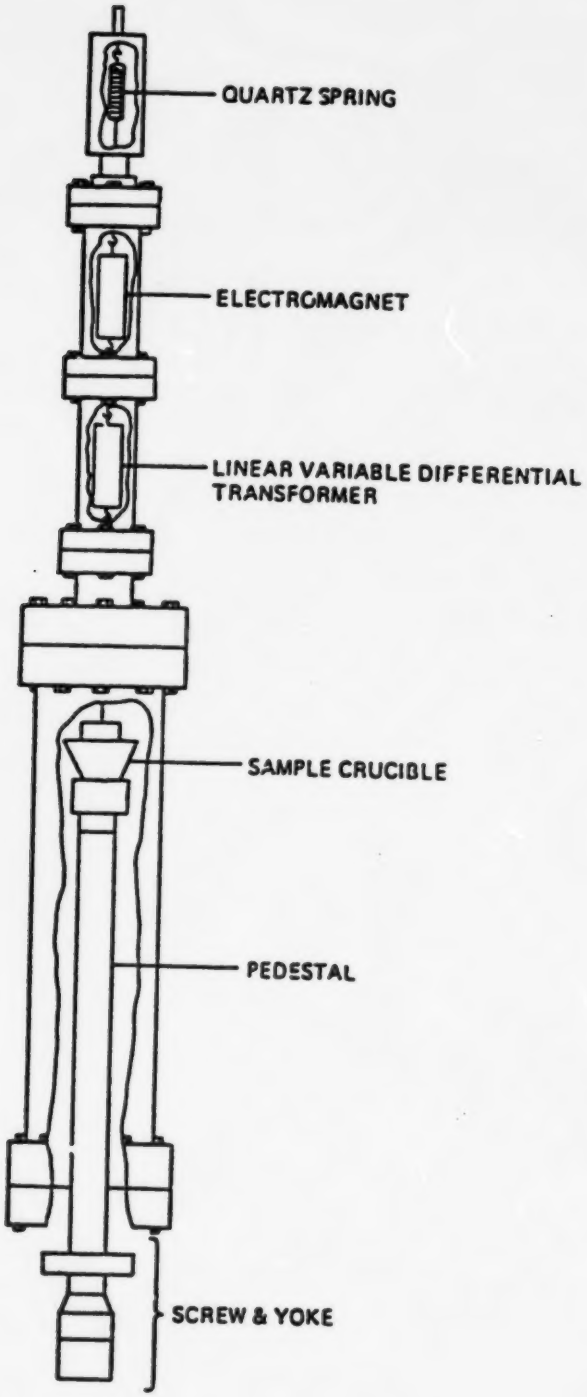

Figure 6 Viscometer Assembly (Cutaway)

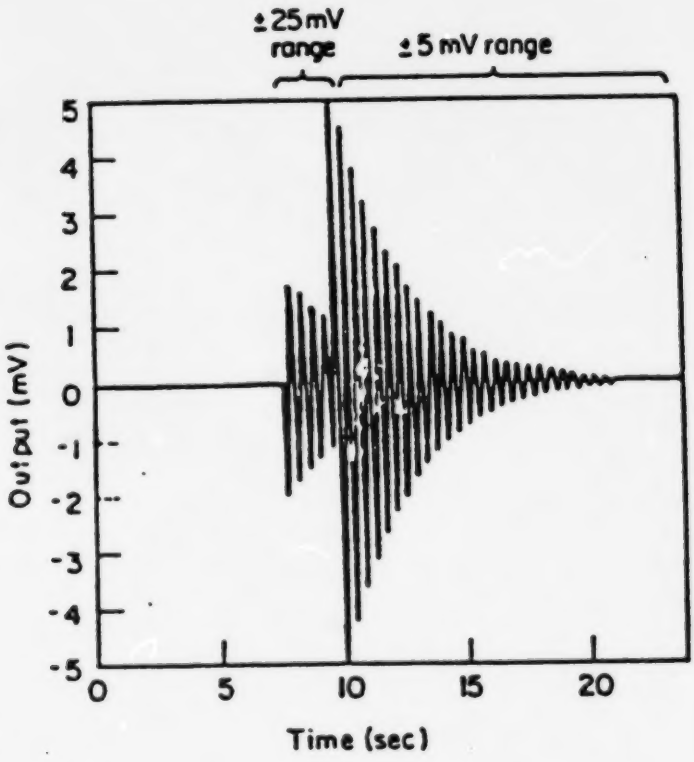

Figure 7 Typical Chart Recording of LVDT Output (for n-amyl alcohol at 66.7 bars, 23°C)

equation is

$$X_{n+1} = X_1 \rho^{-\delta n} \tag{4}$$

where X_{n+1} is the amplitude of the n+1'th and X_1 that of an arbitrary first oscillation. The logarithmic decrement δ is related to the viscosity η and density ρ of the fluid by

$$(\eta\rho)^{1/2} = D\delta - E \tag{5}$$

where D and E are apparatus constants which are best determined by calibration using a known fluid. The simplicity of the measurement lends itself to easy automation and control by a microprocessor. Measurements with such systems have been reported for temperatures up to 600°C and pressures to 12 Kbar, with accuracy $\gtrsim 0.1\%$.

Equation (5) shows that density measurements will be necessary. The virtue of this apparatus is that it is readily converted for use as an Archimedean balance by simply replacing the thin plate by a body of appreciable volume (preferably cylindrical). The loss in weight on immersion in the fluid is given by $(\rho - \rho_g)V_b$ where ρ_g is the gas density and V_b the volume of the body, corrected for thermal expansion. The loss in weight is measured by the extension of the spring in its elastic regime under non-oscillatory conditions.

Other advantages include the small sample size which considerably simplifies the problem of temperature control, so critical for viscosity measurement. Furthermore it is possible to effect some degree of stirring in the event that study of suspensions may be desirable. Finally the assembly is also easily modified for static surface tension measurement by replacing the thin plate with a piece

of screen, or a more suitable plate and using the apparatus for a force balance when the plate is slowly withdrawn from the liquid. The time required for this measurement and the range of movement required make the apparatus unsuitable for dynamic surface tension measurements, however (see also references S-19 and S-20).

All these considerations make this method a clear first choice. If a slightly simpler and more robust instrument is desired the rolling ball method is recommended.

7.0 EFFECTS OF FLUID STATE ON VISCOSITY

(a) **Effect of Temperature:** Viscosity is a very strong function of temperature for most if not all liquids, the effect being greater for liquids of higher molecular complexity. The influence of temperature can be described roughly by two effects. First there is a direct influence of temperature on molecular kinetic energies and secondly there is the influence of density which also changes with temperature, and is, besides, a function of pressure.

Under isobaric conditions or for the saturated liquid, the most common correlation is the well-known Andrade equation

$$\log \eta = A+B/T \quad (T \text{ is absolute temperature}) \qquad (6)$$

where, for a pure compound, A has the same order of magnitude as the log of the viscosity and B is approximately equal to the heat of fusion divided by the gas constant. Generally data at two points allow A and B to be determined. While many more complicated correlations have been proposed, the simple Andrade relation works reasonably well, even for mixtures like petroleum crudes, over temperature ranges $\cong$ 100°C [V6].

There have been only a few methods developed for prediction of viscosity at any temperature given only a single measurement at one temperature. One such is that due to Lewis and Squires [V6, V7] who published the generalized chart shown in Figure 8. In the example shown the viscosity of a crude is estimated as 0.67 cP at 123.8°C given the measured value of 4.38 cP at 22.2°C, the temperature

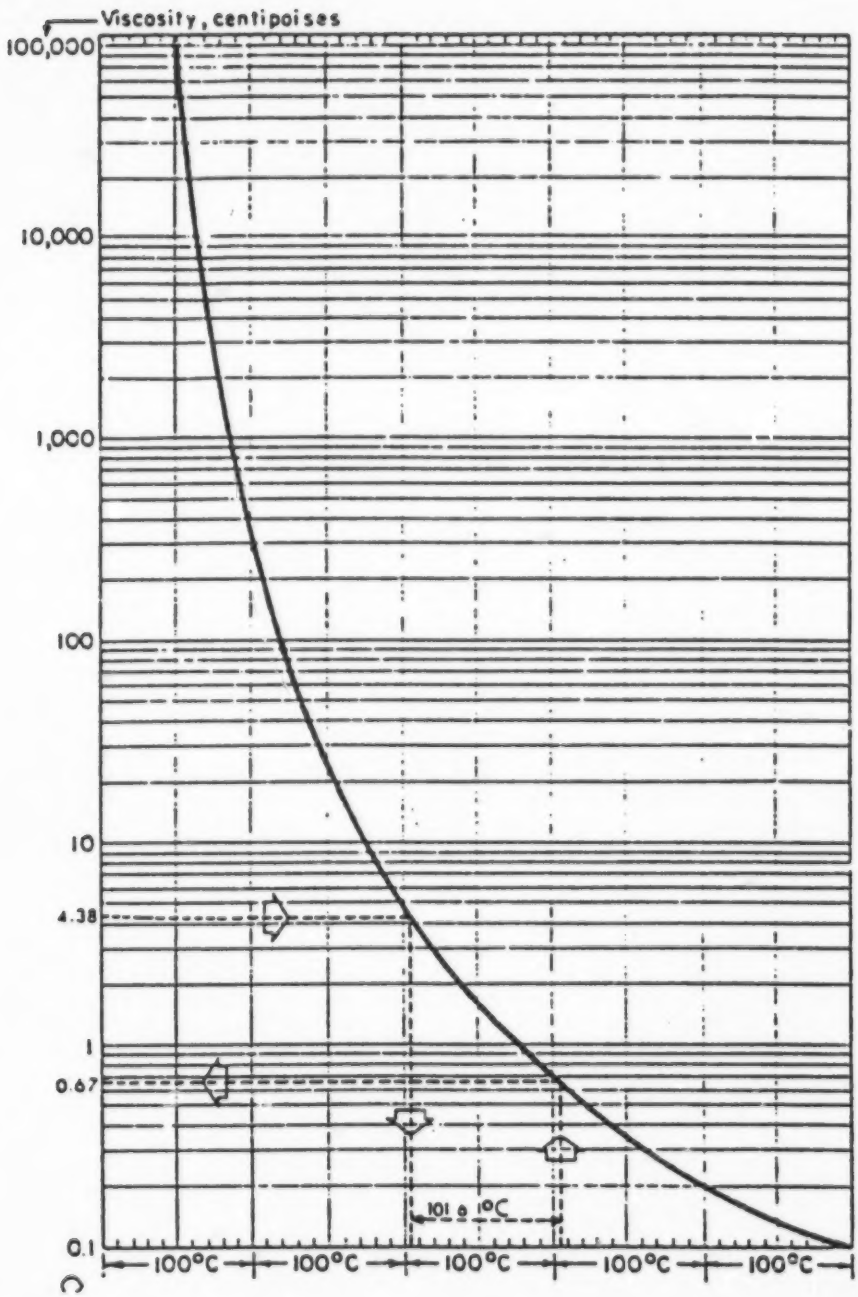

Figure 8 —Generalized viscosity-temperature correlation graph for use when only one value of viscosity is known. Arrows shown refer to the example in the main text. (Courtesy Chemical Engineering).

interval being 101.6°C. Errors may be as high as 20%.

Special methods have been developed for petroleum oils. Most commonly these are based on Walthers double exponential relationship for kinematic viscosity, γ , :

$$\log \log (\gamma+C) = a+b \log T \qquad (7)$$

where C may be a function of γ. One particular version is that due to Wright [V8, V9] and adopted as ASTM Method D341-77 for the prediction of the temperature dependence of the viscosity of petroleum fraction blends.

In these methods the conversion of kinematic to absolute viscosity will require a prediction for the density as well and this is affected by the pressure. Reasonably successful methods for this have been described by Hwang et al. [V1] in an application to coal liquids. Under isobaric conditions a simple linear correlation

$$\rho = a-bT \qquad (8)$$

appears to be adequate.

(b) **Effect of Pressure:** It has already been mentioned that pressure does not exert a strong effect on absolute viscosity and that this is primarily through its influence on density. The variation of viscosity with pressure along an isotherm is in fact essentially linear at pressures up to several thousand bar. At even higher pressures the exponential relationship

$$\log \eta = aP+b \qquad (9)$$

is quite adequate. Generally sensitivity to pressure increases with

molecular complexity.

(c) **Effect of Dissolved Gases:** Dissolved gases generally diminish the viscosity of liquids. If the concentration of gas in the solutions is known then methods developed for mixtures may be readily applied. Hwang et al. [V1] discuss calculations for viscosities of coal liquids containing dissolved hydrogen.

It should be noted that while the viscosity of the saturated solution decreases with pressure (since increased pressure results in increased mole fraction of gas in the saturated solution) the viscosity increases with pressure at constant mole fraction. This is illustrated by some data from Kuss [V10] shown in Figure 9. In each case the uppermost curve represents the viscosity of the pure paraffinic oil while the lower curve represents that of the saturated solution at each pressure. Curves of constant gas mole fraction X_G in the unsaturated region complete each diagram. (Kuss has also proposed a new type of diagram for predicting the influence of temperature on the viscosity of gas/oil solutions [V10].)

(d) **Effect of Suspended Solids:** Addition of suspended solids always increases the viscosity η_s of the suspension over that, η, of the pure liquid. For spherical particles the classical relation is that due to Einstein:

$$\eta_s = \eta(1+2.5\ C) \qquad (10)$$

where C is the volume fraction of solid. This has been found useful up to $C \approx 0.05$. For C up to 0.30 the alternative relation

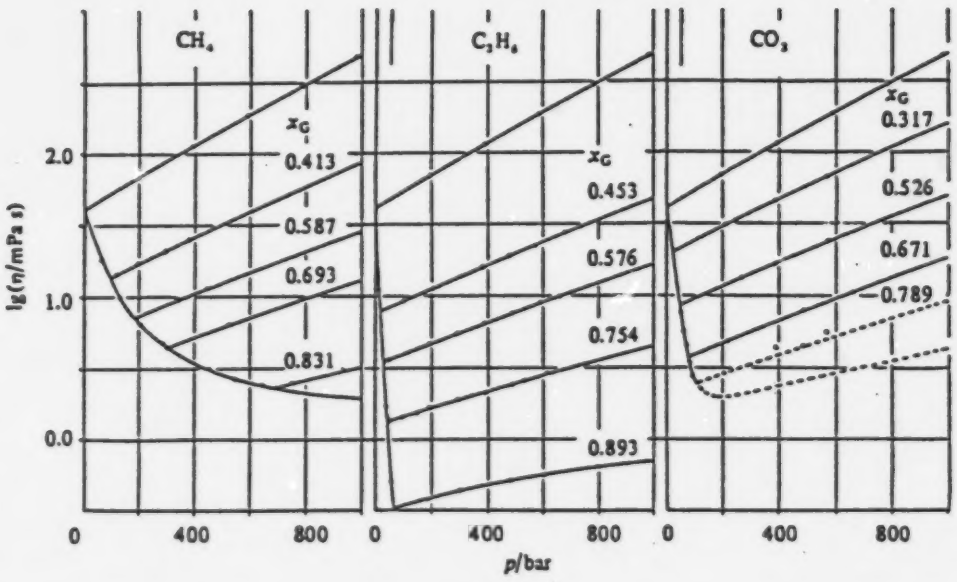

Figure 9

Complete viscosity-pressure diagrams of paraffinic oils with CH_4, C_2H_6, and CO_2 at 40 °C.

$$\eta_s = \eta/(1-KC) \; ; \; 2.65 \leq K \leq 3.15 \qquad (11)$$

appears to work well for various solids including pulverized coal [V11]. More recently, the relation

$$\eta_s = \eta(1-C)^{-m} \qquad (12)$$

where m is a function of the shape of the solid particles has been found useful up to C = 0.40 [12]. Non-Newtonian effects will generally begin to become appreciable at C > 0.25. Furthermore the viscosity will become independent of shear rates only at rates $\gtrsim$ 30 s^{-1}.

8.0 CONCLUSIONS AND RECOMMENDATIONS

On the grounds of accuracy, ease of use and simplicity of construction the linear oscillation viscometer is the preferred method for this application. Other advantages include the ability to use the same apparatus to measure fluid density and the possibility of its use for suspensions. The rolling ball method is the second choice. It is also simple to construct and use. However it requires more extensive calibration and besides it would be necessary to have other equipment for measurement of liquid density.

There are a number of useful correlations available for the prediction of the variation of viscosity of crude oils with temperature. The less sensitive dependence of pressure and suspended solids are rather easily correlated. The effects of dissolved gases in unsaturated solution can be handled by the usual methods for liquid mixtures.

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Excerpt from Reference S-28

In Run 302 an attempt was made to reproduce the gas voidage profile of Run 301 by simply increasing the liquid throughput in the column. Figure 2 shows that by increasing the liquid velocity from 0.0021 to 0.0028 m/s the results of the gas jet experiment were duplicated. Although the superficial liquid velocity was increased by 33%,the decrease in overall gas hold-up resulted in an increase of only 18 % in the liquid hourly space velocity.

Run 303 was caried out to determine whether the foam layer reduction observed during the gas jet experiments was a result of inreased foam drainage rate at the bottom of the foam layer, or discharge of foam at the top of the column as a result of increased gas hold-up in the region of the gas jet. Figure 3 shows the sequence of events during gas jet operation. The column was operated in batch mode (U_G=0.032 m/s, U_L=0) to aid visual observations. With the gas jet shut off there was a foam layer 3.4 m deep. When the jet was turned on the interface moved upwards slightly and the top of the foam layer dropped 0.5 m, resulting in a foam layer 2.7 m deep. With the gas jet still operating, liquid was pumped to the column to bring the top of the foam layer back to the overflow position. The net result of the gas jet operation was a reduction in foam depth of 0.5 m, which is comparable to earlier observations with gas jet and liquid flow. Notice that the ratio of foam depth to column height

(H_F/H_C) was approximately 0.56 with the gas jet while H_F/H_C=0.65 without the jet. Earlier experiments with Varsol 3 indicated that H_F/H_C for batch operation was constant at 0.65 regardless of column height (see Table 1).

TABLE 1

Effect of Column Height on Foam Layer Depth

U_G=0.034 m/s, U_L=0
(All heights in meters)

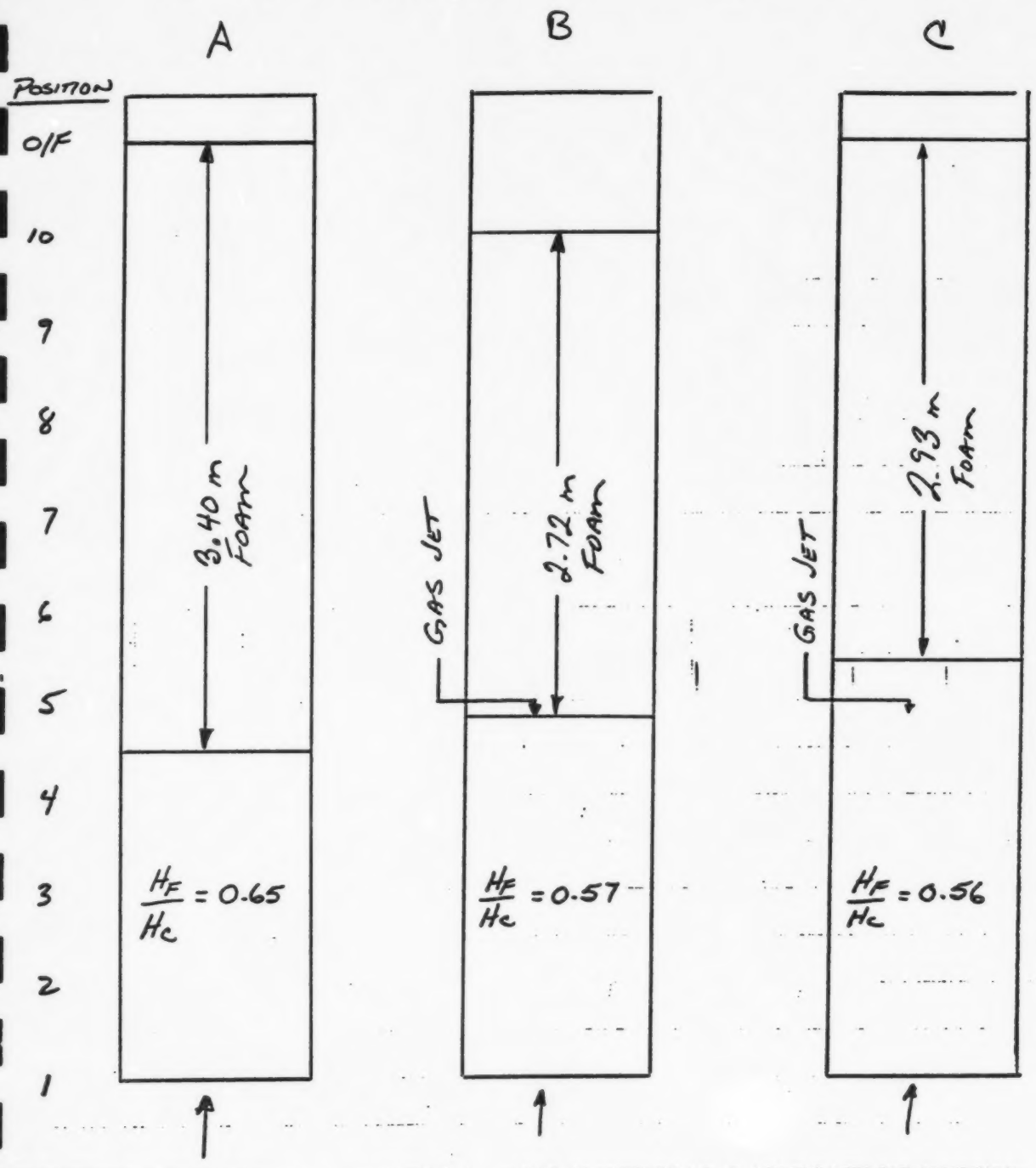
H_C	H_F	H_L	H_{SL}	HOLD-UP	H_F/H_C
1.67	1.05	0.62	0.59	0.65	0.63
2.93	1.88	1.05	1.11	0.62	0.64
3.88	2.60	1.28	1.44	0.63	0.67
4.81	3.17	1.65	1.88	0.61	0.66
5.26	3.40	1.86	2.05	0.61	0.64

H_C=Column Height
H_F=Foam Depth
H_L=Height of liquid below interface
H_{SL}=Height of stagnant liquid

The gas jet was also placed near the top of the foam layer (position 9) during Run 303 and was found to have no effect on foam depth. In Run 304 an additional 15% of gas was added through the main sparger and did not result in a reduced foam layer. From the results of Runs 303 and 304 it was concluded that the gas jet was not acting as a foam breaker as had high shear jets in earlier tests. It is thought that gentle bubbling near the interface promotes increased drainage of foam into the bulk liquid below the

FIGURE 3

RUN #303 - AIR/VARSOL 3/NO SOLIDS



$\bar{U}_G = 0.032$ m/s
$U_L = 0$

$\bar{\varepsilon}_G = 0.61$

$\bar{U}_G = 0.032$ m/s
$U_L = 0$

$\bar{U}_G = 0.032$ m/s
FILL WITH LIQUID TO BRING TOP TO POS. 11
$\bar{\varepsilon}_G = 0.56$

D) START WITH CASE A, WITH GAS JET AT POS. 9 ⇒ NO EFFECT.